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COLLABORATIVE STUDY
of
REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE (HIGH VOLUME METHOD)

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Ralph E. Childers
Oscar Saenz, Jr.

Contract CPA 70-40
SwRI Project 21-2811

Prepared for
Office of Measurement Standardization
Division of Chemistry and Physics
Air Pollution Control Office
Environmental Protection Agency

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16. Abstracts

A collaborative test was conducted involving 12 laboratories. A statistical analysis of the data obtained provided the following results: the relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent; the relative standard deviation for multilaboratory variation (reproducibility of the method) is 3.7 percent; and the minimum detectable amount of particulate matter is 3 mg (95 percent confidence level). This is equivalent to 1-2 $\mu g/m^3$ for a 24-hr sample. Values this low will rarely, if ever, be observed in the atmosphere, and thus lack of sensitivity does not limit the use of this method for ambient air quality measurement. The method can give very good precision when followed rigorously. At the same time, it is rugged, and variations in procedure and technique can occur with only a minor effect on the results. The publication of this method in the Federal Register, April 30, 1971, is appended.

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Approved:

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SUMMARY AND CONCLUSIONS

This report presents information obtained in the evaluation and collaborative testing of a method to measure the mass concentration of suspended particulate matter in the atmosphere. Minor variations of this method have been used extensively by the National Air Sampling Network and by state and local air pollution control agencies for approximately 15 years.

This method was recommended as a tentative standard method by the Intersociety Committee, a cooperative group consisting of representatives of eight scientific and engineering societies.* It was published as Tentative Method 11101-01-70T in **Health Laboratory Science**, October 1970, pp 279-286. It was then tested as a part of this program, by means of a collaborative test involving 12 laboratories. A statistical analysis of the data obtained provided the following results:

- The relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent;
- The relative standard deviation for multilaboratory variation (reproducibility of the method) is 3.7 percent; and
- The minimum detectable amount of particulate matter is 3 mg (95 percent confidence level). This is equivalent to 1-2 $\mu g/m^3$ for a 24-hr sample. Values this low will rarely, if ever, be observed in the atmosphere, and thus lack of sensitivity does not limit the use of this method for ambient air quality measurement.

These results show that the method can give very good precision when followed rigorously. At the same time, it is rugged, and variations in procedure and technique can occur with only a minor effect on the results.

Based on these results, this method was adopted as a standard method for the measurement of suspended particulate matter in the atmosphere by the Standardization Advisory Committee of the Air Pollution Control Office, Environmental Protection Agency. It was published in the *Federal Register*, April 30, 1971, and is reproduced as Appendix A of this report.

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* Air Pollution Control Association
American Chemical Society
American Conference of Governmental Industrial Hygienists
American Industrial Hygiene Association
American Public Health Association
American Society for Testing and Materials
American Society of Mechanical Engineers
Association of Official Analytical Chemists

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The assistance and cooperation of the participating laboratories is also acknowledged with sincere appreciation for the voluntary efforts of the staff members who represented each organization. The representatives and organizations participating in the collaborative test program were as follows:

Name	Organization
Harold K. Beatty	Department of Environmental Control Chicago, Illinois
J. H. Blacker	Esso Research and Engineering Co. Linden, New Jersey
Walter W. Cooney	State of Maryland Division of Air Quality Control Baltimore, Maryland
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Frank G. Norris	City of Steubenville Air Pollution Department Steubenville, Ohio

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I. INTRODUCTION

Of all the various methods available to measure atmospheric contaminants, the so-called High Volume Method (frequently called "Hi Vol" Method) has probably been used more extensively than any other. One reason for this is the widespread occurrence of dust and particulate matter in the atmosphere, with measurable quantities occurring as natural background even in remote areas. Another reason is that the equipment required is relatively inexpensive, whereas the measurement of other contaminants may require much more expensive and elaborate instruments. First developed by the predecessor organization of the present EPA Air Pollution Control Office in the mid-1950's, this method has been used on a large scale by the National Air Sampling Network for approximately 15 years. Many state and local air pollution control agencies have also used this method, or variations of it, for monitoring networks to supplement the Federal effort.

The High Volume Method can be used by any laboratory possessing normal equipment and skills if a minimum of special purpose equipment is added. A sampler capable of pulling air through a filter medium is used to collect the dust and particulate matter, which is then measured on a weight basis. Chemical analysis of the collected deposit is also possible to measure various constituents such as metals, nitrate, sulfate, etc. (Analytical procedures for such analyses are not included in this standard method at the present time.)

Since no standardized procedure has been available to guide different laboratories in the use of this method, each laboratory has had to develop and evaluate different techniques for weighing filters, calibrating flow rates, and other details in conducting tests. As an example, only 40 percent of the collaborators in this test were routinely using a procedure essentially similar to the method tested. Less than half had access to a positive displacement meter to use as a primary standard for calibration. While 80 percent had some sort of orifice calibration unit, only 10 percent indicated that it was ever calibrated using a primary standard of any kind. The calibration of a sampler was indicated to be a standard practice; however, only 20 percent calibrated routinely on a monthly basis and 40 percent on a yearly basis. The remaining 40 percent did not calibrate on any predetermined schedule.

In order to obtain comparable data so that interlaboratory comparisons would be feasible, the Air Pollution Control Office has been working for some time to develop standard methods which could be used by all persons making air quality measurements. A number of scientific and engineering societies have also been active in the development of standard methods, including several of those now participating in the Intersociety Committee, whose members are listed in the Summary and Conclusions.

Following the development of a tentative standard method by the Intersociety Committee, the final step in the standardization process is to conduct a collaborative test, or interlaboratory comparison, of the proposed standard method. This procedure, also called "round-robin testing," has been used to evaluate many different methods of measurement in such diverse fields as water chemistry, metallurgy, paint and surface coatings, food and related products, and many others. A test of this nature by a representative group of laboratories is the only way that the statistical limits of error inherent in any method can be determined with sufficient confidence.

This report presents the results of a collaborative test of the High Volume Method conducted by Southwest Research Institute and the Air Pollution Control Office, together with the statistical analysis of the data obtained. In planning for the collaborative test, it was necessary to evaluate several aspects of the recommended method with respect to flow rate calibration and other details. The information obtained in this evaluation is also presented as background information relating to the collaborative test program and as information helpful in understanding the capabilities and limitations of this standard method.

II. EVALUATION OF THE METHOD

Since the High Volume Method has been used by many laboratories, it is not surprising that many different variations of this method have occurred, especially in flow rate calibration and other details of measurement. To aid in resolving some of these differences, an evaluation of the method was performed during the development of plans for collaborative testing. This section of the report presents the data obtained in some of these tests and discusses the importance of different procedures in planning a collaborative test and in evaluating the capabilities and limitations of the method itself.

A. Calibration of Flow Rate

In calibrating the flow measuring system of the sampler, it is necessary to vary the flow rate over the operating range of the sampler in order to obtain accurate calibration. In the past, most workers have done this by either of two methods: (1) use of a series of perforated plates in place of the filter used for sample collection, to vary resistance to flow (as presently shown in the method); or (2) use of a variable transformer to change the voltage applied to the blower motor, thus varying the speed of the blower and changing the flow rate. However, recent work[(1)]* indicated that varying the speed of the blower led to possible errors, especially at low flow rates, because this changed the flow pattern through the sampler, which in turn caused changes in the flow pattern past the variable-orifice meter located on the discharge side of the blower. Therefore, both procedures were evaluated to see if errors would occur with the method of calibration specified in the proposed method.

Two types of high volume samplers were checked. The first was equipped with a rotameter for flow measurement, and the second had an orifice on the discharge side of the blower for continuous recording of flow rates. With both types of sampler, flow rate was varied by using resistance plates, as specified in the method, and by using a variable transformer to vary the speed of the blower. No differences were observed with the sampler equipped with a rotameter for flow measurement. Identical readings were obtained throughout the range of flow rate (30 to 65 cfm), regardless of whether the flow was varied by using the resistance plates or by controlling blower speed. With the other sampler, however, this was not the case. Identical readings were obtained at the higher flow rates, but at lower flow rates a difference was observed. In all cases, the indicated flow was lower when the voltage was varied than when the resistance plates were used. The differences were not great, ranging from 2 cfm at the low rate of 30 cfm to no difference at 60 cfm. However, this confirmed the fact that some error may occur with this method of calibration, as was indicated by the University of Cincinnati results, and, therefore, the Intersociety Committee deleted the optional calibration procedure based on voltage variation. The use of resistance plates was specified as the standard method of varying flow during calibration and is included in the method as now published. This method was used during the collaborative test of the method.

B. Selection of Sampling Locations

A standard method can be developed to specify details of calibration, flow measurement, analysis of samples, etc., in considerable detail, and the statistical accuracy of these various procedures can be established. In the measurement of total particulate matter, however, a serious problem exists which is not subject to statistical evaluation, except in rather general terms. Since particulate matter is a ubiquitous constituent of the atmosphere, and, since the amount varies widely from place to place, the selection of sampling times and locations is a matter of paramount importance. This cannot be standardized in a specified method, but some general guidelines can be given to indicate how these factors will influence the results obtained.

Measurements of total particulate matter by the High Volume method are usually made to determine

*Superscript numbers in parentheses refer to the List of References.

overall community-wide patterns which exist. However, if the results obtained in any one location are influenced to a major degree by a significant source of dust located nearby, then the results will be typical of dust levels over an extremely small area rather than the portion of the community which a particular monitoring station should represent.

This means, then, that if a monitoring station is intended to represent typical levels over a large area, it should be placed in a location free of local interferences. The most obvious interferences to avoid are unpaved streets and parking lots, a major dust-emitting industrial plant that would constitute a single dominant source, nearby construction activities, and other obvious sources which affect only limited geographical areas.

No specific figures can be given for the amount of interference which such sources can cause since this may vary over many orders of magnitude, depending on the nature of the source and on the distance from the source to the sampling location. However, samples showing several hundred or even a few thousand micrograms per cubic meter ($\mu g/m^3$) have been collected directly downwind from obvious sources of this nature[2,3], which indicates that values can be obtained which are several times the community-wide levels that usually exist.

Another important variable in some circumstances is the height of the sampler above the ground. Dust raised by automobile traffic and other extraneous sources frequently contains a large proportion of relatively large particles which settle back to the earth fairly rapidly, and therefore would not be collected by a sampler located some distance above the earth's surface. In one study[2], for example, samples were collected 3 ft and 30 ft above ground level next to a paved street with a light deposit of dust on the surface of the pavement from nearby construction activity; values obtained at the upper level averaged about 50 percent of those obtained at the lower level. In another study[3], 24-hr samples were collected in four cities at levels of 3 ft and 30 ft; in this case, average values for the four locations indicated that samples collected 30 ft above ground level showed from 60 percent to 90 percent of the dust loadings measured 3 ft above ground level.

If samples are obtained for less than a 24-hr period, the time of day is also an important variable. This is illustrated by samples collected at 3-hr intervals which show very low levels at night, occasionally in the range of rural background levels such as 20 to 40 $\mu g/m^3$. During daylight hours, however, values are usually much higher due to vehicular traffic and other human activities, frequently reaching 3-hr levels as much as four to five times the nighttime values.[4] This shows the desirability of collecting 24-hr samples to evaluate overall conditions in the community.

As stated previously, no specific standard procedures can be given to compensate for these problems. However, a considerable degree of judgment and experience must be utilized in the selection of sampling locations and in the evaluation of data to avoid reaching erroneous conclusions because of nearby sources of dust which may exert an undue influence on sampling results. Since the objective of a monitoring network usually is to determine community-wide levels, sampling locations should be chosen to avoid excessive influence from a single dominant source immediately adjacent to the sampler.

To conduct a collaborative test, results were needed which would be representative of particulate levels over a considerable area and which would not be unduly influenced by a single source. As discussed later, a location was selected which appeared to meet this requirement.

C. Effect of Possible Volatilization

As outlined in the method, filters should be equilibrated in the laboratory for 24 hr prior to weighing, or reweighing after sampling, to determine the weight of material collected. During the preliminary sampling prior to collaborative testing, filters were kept and reweighed after succeeding intervals of time to obtain some information on possible changes.

TABLE I. SUMMARY OF PRELIMINARY DATA FOR SAMPLING OF PARTICULATES AND THE EFFECT OF EQUILIBRATION TIME

Particulate Concentration, $\mu g/m^3$

Sampler Number*	First Day Equilibration Time		Second Day Equilibration Time		Third Day Equilibration Time	
	1-Day	4.5-Day	1-Day	4.5-Day	2-Day	5.5-Day
1	95	89	80	75	82	76
2	100	88	73	69	73	69
3	85	76	82	75	83	79
4	96	83	83	76	77	73
5	92	82	80	76	82	78

*Samplers at a different location on the roof each day.

Table I tabulates the results of these tests. After an additional 3.5 days of equilibration, the indicated concentration of particulate matter had decreased by 5 percent or more. It is presumed that this was due to evaporation of volatile "tarry" organic materials or loss of water from the filters, with the tarry materials being the more probable explanation. No completely satisfactory method exists to compensate for these changes, but this factor emphasizes the importance of observing the 24-hr time limit specified in the method if the results are to be comparable from one series of tests to another. If the presence of volatile impurities is suspected of causing any significant variation in sampling results, separate investigation of this factor would be advisable.

While the exact cause has not been determined, greater amounts of tarry materials would be expected if the particulate sample contained a substantial amount of coal smoke, smoke from an operation such as a hot mix asphalt plant or coke oven, particulates from vehicle exhaust, or other materials that would likely be high in organic content. Much smaller losses would be expected in areas where the primary constituents of atmospheric particulates would be natural soil particles, dust from sandstorms, or other materials of mineral origin.

Since the preliminary evaluation indicated a possible source of error due to loss of weight after sample collection, this factor was also considered in conducting the collaborative test. The results are discussed subsequently in outlining various considerations which may affect the precision of the standard method.

III. COLLABORATIVE TESTING OF THE METHOD

An important step in the standardization of any method of measurement is the collaborative testing of a proposed method to determine, on a statistical basis, the limits of error which can be expected when the method is used by a typical group of investigators. The collaborative, or interlaboratory, test of a method is an indispensable part of the development and standardization of an analytical procedure to insure that (1) the procedure is clear and complete, and (2) the procedure does give results whose precision and accuracy are in accord with those claimed for the method.[5] Among other organizations, the American Association of Analytical Chemists (AOAC) and the American Society for Testing and Materials (ASTM) have been active in the field of collaborative testing and have published guidelines of the proper procedure for conducting collaborative tests and evaluating the data obtained.[6-8] Publications of both of these organizations were used extensively in planning and conducting the collaborative test of this method to measure atmospheric particulates.

After the preliminary evaluation of the proposed method had been completed and various questions regarding procedure had been clarified, a detailed collaborative test was undertaken to obtain the necessary data to make a statistical evaluation of the method. This section of the report describes the test plan that was developed, presents the data obtained, and provides a statistical analysis of the data, together with conclusions based on the results and statistical analysis.

A. Selection of Collaborators

If a collaborative test is to achieve the desired objectives, it is necessary that the participants in the collaborative test be representative of the large group that will ultimately make use of the method being tested. Since air pollution measurements are of interest to many different groups, it was desirable to include in the group of collaborators a variety of

governmental agencies, universities, industrial laboratories, and others. The final selection included three participants from federal laboratories, five from state and local air pollution control agencies, one from industry, two from universities, and one from a research organization. A complete list of the participants and their affiliation is given elsewhere in this report.

Each laboratory that agreed to participate was asked to select a staff member with previous experience in measuring particulates by the high volume sampler method. This was done to avoid errors that otherwise would result from lack of experience, and thus provide a more realistic appraisal of the capability of the method being tested. Each laboratory also was engaged in making routine measurements with this method or some variation of the same method, and possessed the necessary equipment for calibration of samplers, conditioning and weighing of filters, and other work necessary to follow the method as outlined.

B. Planning the Test Series

Ideally, a collaborative test should be conducted by a group of participants, each working in his own laboratory in his usual manner. For some methods to measure air pollution, this can be accomplished by sending known samples to various laboratories for analysis. In this case, however, no method was available to send a "standard atmosphere" which could be used for test purposes, and, therefore, it was necessary to make measurements by sampling a real atmosphere. In order to assure uniformity, the participants were brought together to one location to sample the same atmosphere simultaneously. A laboratory building used by the Air Pollution Control Office in Cincinnati, Ohio, was selected where a large area on the roof of a two-story wing of the building provided adequate space. A clear space approximately 50 × 100 ft was available without obstructions. An exhaust fan outlet on the roof was equipped with a duct which discharged the exhaust air down below roof level along the side of the building so that no disruption of normal atmospheric turbulence would occur. This location was also convenient in that laboratory facilities were available in the same building to provide a work area for calibration and assembly of equipment.

The building chosen was located in a neighborhood which contained both residential and industrial property. Several industrial plants in the area produced visible emissions, although none were located close enough to the site so that a dominant effect from a single source would be expected. Cincinnati is also in an area where coal is used extensively as fuel, and thus some coal smoke would be included in the atmospheric particulates present. The nearest freeway with heavy traffic was several hundred yards distant. By sampling on top of a two-story wing of the building, localized effects from vehicle traffic in the immediate neighborhood would be minimized. Thus, all preliminary evidence indicated that this site was typical of many urban locations that might be used for air pollution monitoring, and would be expected to give results representative of particulate levels over a wide area of that portion of the city. Subsequent experience in the collaborative test appeared to confirm this expectation, and, therefore, the area of the test site was considered to be well suited to the objectives of the test.

In order to minimize any effects which might result from working in unfamiliar surroundings, each participant was instructed to calibrate the sampler, condition and weigh all filters, and do all other preparatory and followup work in his own laboratory. Work in Cincinnati was then to be limited to rechecking the flow rate and to actual sample collection. Thus, insofar as possible, the final results should indicate what each participant routinely accomplishes in his own laboratory. In the original schedule, time was allowed for rechecking sampler calibration in Cincinnati prior to sampling, to be sure that shipping of equipment had not adversely affected the calibration. However, it was found that many laboratories did not have access to a positive displacement meter to use as a primary calibration standard and other laboratories did not use the standard type of orifice meter for calibration. Therefore, the entire

calibration procedure specified in the method was repeated by all participants after arrival in Cincinnati, including both the calibration of the orifice meter with a primary standard and the calibration of the sampler with the orifice meter.

C. Site Evaluation

In order to be sure that the site chosen for the collaborative test was suitable, a preliminary evaluation of this particular site was performed prior to the actual test. The primary objective of this work was to confirm the fact that all samplers used in the test would be sampling the same atmosphere. For this purpose, five samplers were placed in representative locations on top of the building and were operated for three sampling periods of approximately 24 hr each. While some variation occurred among samplers, as expected, there was no systematic pattern which would indicate a consistent difference in atmospheric dust levels. The data are shown in Table I and indicate that location within different sections of the roof area was essentially immaterial in affecting the particulate levels measured. Therefore, when 12 samplers were used simultaneously during the actual test, it could be assumed that all participants were measuring the same test atmosphere.

Another factor considered in evaluation of the site was the location of the 12 samplers, within the clear space available, when the collaborative test was conducted. It was decided to use two rows of 6 samplers each, maintaining a 12-ft spacing both ways between samplers. With this arrangement, no sampler was placed closer to the edge of the roof than 12 ft, thus avoiding turbulence and other flow disturbances that might exist at the edge or corner of the building. In the preliminary tests, a 12-ft spacing was used with 2 of the 5 samplers, and the results indicated that no interference resulted. In fact, a superficial examination of airflow patterns around a sampler indicated that any disturbance of airflow was dissipated rapidly, and interference with an adjacent sampler would not be expected unless a spacing of 3 ft or less was used. Therefore, all available evidence indicated that the site and the proposed arrangement of samplers were adequate for the purposes of the test.

D. Conducting the Test Series

Actual sampling at the Cincinnati site was accomplished in a single week in October 1970, from Monday morning to Friday afternoon. Weather conditions during the week were variable, covering the normal range of conditions expected at that season of the year. Light rain fell during portions of the second and third day. The morning period on Monday was used by all participants to unpack equipment, calibrate orifice meters and samplers, and set up shelters. The first sampling period was started in the afternoon on Monday when all participants were ready.

All samplers were started simultaneously for the actual sampling period and each participant observed and recorded the initial flow rate. At the end of each sampling period (approximately 24 hr), each participant determined the final flow rate and then all samplers were stopped simultaneously. The filters were removed, new filters were installed for the next sample period, and the entire procedure was repeated. While the samplers were running, everyone stayed away from the test site except for occasional checks of equipment, to minimize errors due to dust that might be raised by walking on the roof.

At the conclusion of the final test period on Friday, final flow rate figures were obtained, samplers were stopped, the filters were removed from the samplers, and shelters and other equipment were packed for shipment. Each participant was asked to return the filters to his own laboratory, condition them as specified in the method on Monday and Tuesday (for a total of 24 hr), and then obtain a final weight. This weight was used for calculations and, in addition, subsequent weighings were also made to obtain additional data on weight loss. The question of weight loss over a period of time is discussed in connection with the evaluation of the precision of the method.

One participant lost a sample when the sampler motor brushes failed. However, this person replaced

the brushes and recalibrated the sampler prior to the beginning of the next period, thus limiting the loss to a single sample. This gave a total of 47 samples from all participants out of a possible 48 (12 participants, 4 samples each). Data from these 47 samples were then used for the statistical analysis which was performed.

E. Summary of Statistical Analysis

The fundamental purpose of the statistical design was to determine the existence and amount of both random and systematic laboratory errors. The experiment was designed so that, in addition to interlaboratory comparisons, some implications could be made regarding the day-to-day variations within an individual laboratory. No estimate is possible, however, for replication errors, since a true replicate cannot be accomplished. Since it was impossible to prepare and submit samples with known reference values, no statements regarding the accuracy of the method can be made.

In consideration of the logistics involved, a very comprehensive test is not feasible; however, a modest test design was possible. The approach was to have all collaborators sample from the same real atmosphere at the same site at the same time. There were 12 collaborators, each from a different laboratory, who worked independently but simultaneously at the same site collecting data for 4 consecutive days. Thus, each day constituted a separate sample or material, of unknown concentration, but common to all participants. It should be made clear that there was no intent to measure day-to-day variations for the site. Neither was it desirable that all days be the same, a condition not under experimental control. A single result was collected by each analyst for each of the 4 days, yielding the data shown in Table II. Samples were collected over a 24-hr interval; therefore, no replication was possible for a particular analyst-sampler combination. Although the data do not cover a wide range, they are certainly satisfactory. Notice that there are 2 days with means near 120 micrograms per cubic meter ($\mu g/m^3$) and 2 days with means significantly lower and near 80 $\mu g/m^3$, a fortuitous but agreeable circumstance.

TABLE II. COLLABORATIVE TESTING DATA–HIGH-VOLUME METHOD FOR PARTICULATES

Particulate Concentration, $\mu g/m^3$

Laboratory Number	Day 1	Day 2	Day 3	Day 4
222	138	*	87	114
311	125	80	82	113
320	128	72	81	112
341	126	75	83	114
345	127	78	87	124
509	128	74	86	121
572†‡**	128	82	84	112
575† ††	108	73	72	93
578†	126	77	83	111
600	125	72	80	110
787‡	125	76	83	117
799	131	76	86	120

*Missing data due to equipment malfunction.
†Recalculated results because of errors in units of measurement.
‡Recalculated results because of arithmetic errors.
**Recalculated results because of incorrect data entry for time of sampling.
††Recalculated results because of errors in calibration curves.

The statistical analysis, presented in more detail in Appendix B, is summarized in the following paragraphs.

The standard deviation for each day fluctuated systematically with the respective means, indicating that it was advisable that the data be transformed to a different scale. The appropriate tests were applied, resulting in the use of the simple logarithmic transformation. All subsequent analyses were made on transformed data.

The missing sample for one laboratory required either that all data for that laboratory be rejected or that an appropriate substitution be made for the missing value. The latter approach was followed, as outlined in Appendix B.

Following standardized procedures for the analysis of data of this type, Figure 1 was prepared. This illustration is based on transformed data and shows a separate line for each laboratory, plotting the observed values against reference values equal to the mean of all laboratories for each day. This makes it possible to visualize the grouping of the data and to identify the variation between laboratories. One obvious advantage of this presentation is that any outliers can be easily identified; in this case, it is obvious that the results of Laboratory 575 are significantly different. Other outlier tests also substantiated this

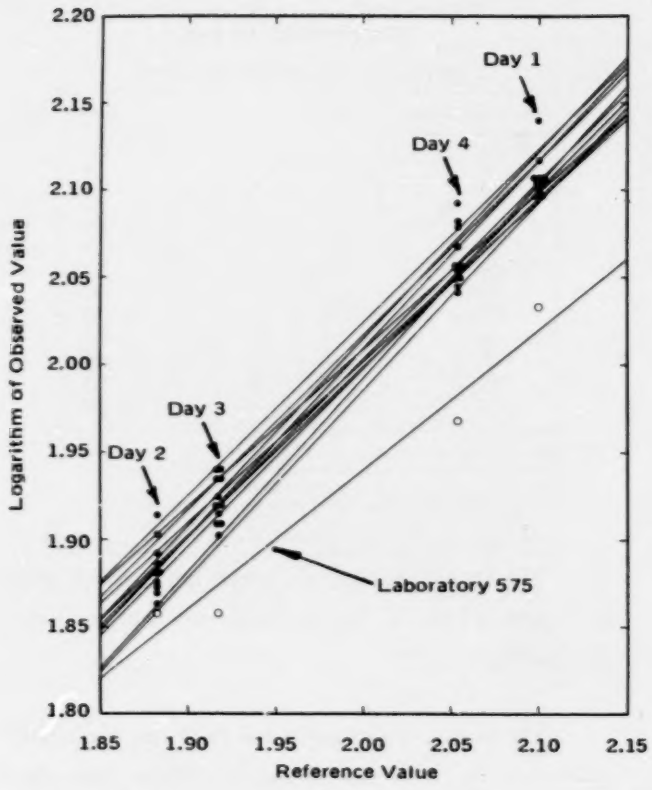

FIGURE 1. GRAPHIC DATA SUMMARY FOR ALL LABORATORIES, LOGARITHMIC DATA TRANSFORMATION

conclusion, and the final statistical analysis was made omitting Laboratory 575.

An analysis of variance of the transformed data for 11 laboratories was made, and the model and more detailed data are given in Appendix B. The ultimate purpose for making the analysis of variance is to derive components of variance which are shown in Table III. The mean square from the deviation from linear term is the component V(d) which contains the unknown replication error plus the irreducible experimental error of the method. Components V(u) and V(b) express the variability of the means and the slopes, respectively, from one laboratory to another. These components were calculated according to recommended practice.(9) A negative value for V(b) was obtained and therefore replaced with a value of zero, since negative variances are meaningless. V(u) is highly significant while V(b), of course, is not significant. The confidence intervals (95 percent level of significance) for each component are shown in Table III. Since the component V(b) is not significant at the 95 percent level of significance, the lower confidence limit is naturally zero.

TABLE III. COMPONENTS OF VARIANCE

Component	Value*	Percent of Total	Significance	Relative Deviation, Percent	
				Estimate	Confidence† Interval
V(u)	0.000087	34	>99%	2.2	0.6 to 4.3
V(b)	0	–	<50%	0	0 to 1.4
V(d)	0.000166	66	–	3.0	2.3 to 4.4

*Based on transformed data.
†95 percent confidence interval.

The quantities V(d), V(u), and V(b) are the basic elements from which the precision of the results can be estimated for any set of conditions.(10) The reproducibility and the repeatability(8) may thus be determined.

Two-thirds of the variance is accounted for by the component V(d). The relative standard deviation for a single material analyzed repeatedly in the same laboratory by the same analyst is 3.0 percent, the repeatability of the method. Any two such values should be considered suspect (95 percent confidence level) if they differ by more than 4.3 percent. Conversely, two materials analyzed in the same laboratory may not be considered significantly different if the results differ by less than 4.3 percent.

One-third of the variance is accounted for by the component V(u). The relative standard deviation for a single material analyzed in different laboratories is 3.7 percent, the reproducibility of the method. Any two such values should be considered suspect (95 percent confidence level) if they differ by more than 5.3 percent. Conversely, two materials, one analyzed in each of two laboratories, may not be considered to be significantly different if the results differ by less than 5.3 percent.

Some additional information was obtained during the collaborative test relating to errors from individual steps within the method. Each collaborator was asked to submit the results of a series of weights of the filters that were supplied. A series of three weights at 24-hr intervals was requested for each of

ten filters provided. These data were obtained by the collaborator prior to coming to the test site. Following the formal collaborative test, each analyst returned to his own laboratory and made a series of four weights, at 24-hr intervals, of each of the ten filters, not all of which were used in the test. The weight after the first 24-hr equilibration was used, as specified by the method, to calculate the total suspended particulate concentrations which were reported.

The supplementary weight data for the succeeding 3 days are useful for two purposes: first, to provide an estimate of a limit of detectability of the method; and, second, to give an indication of the stability of the suspended particulate matter.

These data can be divided into three subsets:

- Unexposed filters prior to test period
- Unexposed filters after test period
- Exposed filters used in the test.

These data indicate the combined random effects of equilibration, weighing, and decomposition or volatilization of particulate matter. The standard deviation of the weights for each of the cases is 0.7, 0.9, and 1.7 mg, respectively. The number of sets of replicates for each case is 100, 56, and 43, respectively. Bartlett's test[11] for homogeneity of variances leads to the acceptance of the null hypothesis that there is no difference between the variances in the weights of the unexposed filters before and after the test period. The variance in the weights of the used filters was shown to be significantly greater than that of the unexposed filters, indicating that there are significant changes in the weights of exposed filters over the 96-hr period.

The data, which are too voluminous to report here, show weight losses up to 10 mg, or about 5 percent, for an individual used filter over the 4-day period of equilibration. This loss, though less than that indicated in the preliminary work, is significant in terms of the precision data reported above. This illustrates the importance of careful control and uniformity of equilibration in order to achieve satisfactory reproducibility. The presence of volatile materials can cause unpredictable errors.

In the absence of significant amounts of volatile material, an estimate of the lower detection limit can be made. The standard deviation of the difference in the mean weights of the unexposed filters before and after the test period could be directly determined for a set of 56 observations. The result obtained was 1.5 mg, which is almost exactly the same value obtained by the less direct method of doubling the standard deviation obtained for all unexposed filter weights. Based upon this result, the 95 percent confidence limit for these differences is 3.0 mg. Therefore, a difference in weight of 3 mg or less cannot be considered to be significantly different from zero. The minimum detectable amount of particulate matter is thus 3 mg, and, for a 24-hr sample at 1.5 cubic meters per minute (53 cfm), this would correspond to a minimum detectable concentration of 1.4 $\mu g/m^3$. A concentration this low will rarely, if ever, be observed in the atmosphere.

F. Calibration Errors

It was possible to investigate the random error associated with the calibration of the orifice units with the primary standard positive displacement meter. The experimental design was such that a participant was randomly assigned one of six identical orifice calibration units and one of five essentially identical positive displacement meters. The participant then calibrated the orifice unit according to the tentative method. These independent calibration curves have been superimposed in Figure 2 which is a log-log plot of the flow rate through the orifice versus the pressure differential across the orifice. With the exception of one laboratory (787) and one atypical point for another laboratory (311), linear results were obtained. Another laboratory (572) switched primary standard meters in the middle of the calibration procedure; however, there were no noticeable irregularities in its results. A least squares regression

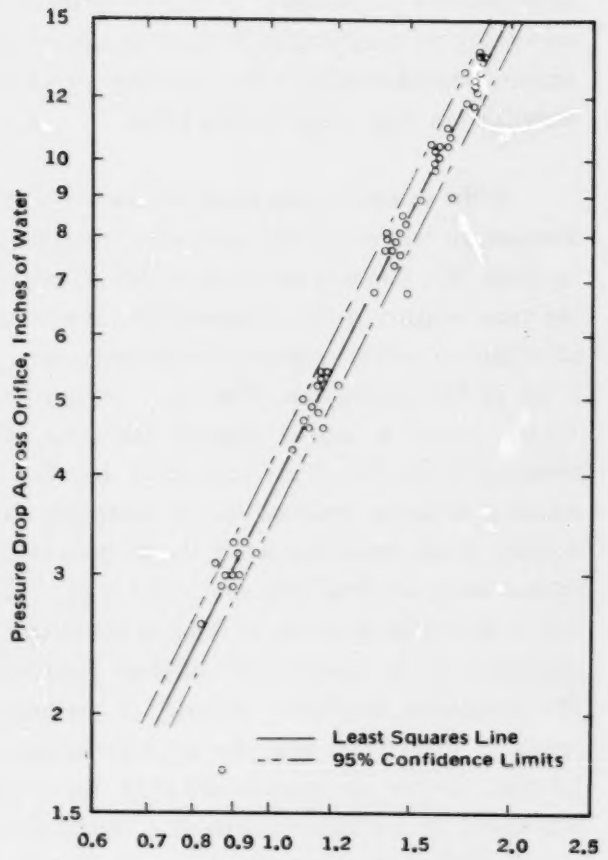

FIGURE 2. ORIFICE METER CALIBRATION DATA

analysis was made (omitting Laboratory 787 and the extraneous point of Laboratory 311) and the line of best fit is shown in Figure 2. The magnitude of the derived constants for the regression line is of secondary importance. The important consideration is the standard error of estimate which is 2.1 percent. This error combines the errors from variation among orifice units, variation among positive displacement meters, and experimental measurement in the calibration procedure. The 95 percent confidence interval for the error associated with calibration is ±4.1 percent. All the orifice units used in the test were new and in good condition.

The manufacturer[12] furnishes an "Average Calibration Curve" with each orifice. The orifice units are quoted as being accurate to ±1.0 percent. These calibration data are almost identical with the line of best fit in Figure 2. The temperature and pressure conditions are approximately the same for each.

It should not be concluded that the calibration of the orifice should be omitted on the basis of these estimates; rather, that the main purpose of periodic orifice calibration is to provide assurance that the orifice has not been damaged or otherwise changed in accuracy. A difference of more than 4 percent from the manufacturer's curve probably means that the orifice has been damaged.

LIST OF REFERENCES

1. Lynam, D. R., Pierce, J. O., and Cholak, J., "Calibration of the High-Volume Air Sampler," *American Industrial Hygiene Association Journal,* No. 30, pp 83-88 (January-February 1969).

2. Unpublished data, Southwest Research Institute, Houston, Texas.

3. Unpublished data, Texas Air Control Board, Austin, Texas.

4. Unpublished data, Air Pollution Control Program, City of Houston Health Department, Houston, Texas.

5. Youden, W. J., "The Collaborative Test," *Journal of the AOAC,* Vol 46, No. 1, pp 55-62 (1963).

6. **Handbook of the AOAC,** Second Edition, October 1, 1966.

7. **ASTM Manual for Conducting an Interlaboratory Study of a Test Method,** ASTM STP No. 335, *Am. Soc. Testing & Mats.* (1963).

8. Recommended Practice for Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals, ASTM Designation: E180-67. 1968 Book of ASTM Standards, Part 30.

9. ASTM STP No. 335, op. cit., p 37.

10. Ibid, pp 37-40.

11. Dixon, Wilfred J., and Massey, Frank J., Jr., **Introduction to Statistical Analysis,** Chapter 10, pp 179-180, McGraw-Hill Book Company, Inc., New York (1957).

12. General Metals Works, Cleves, Ohio.

APPENDIX A

REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE (HIGH VOLUME METHOD)

Reproduced from Appendix B, "National Primary and Secondary Ambient Air Standards," *Federal Register*, Vol 36, No. 84, Part II, Friday, April 30, 1971.

APPENDIX B—REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE (HIGH VOLUME METHOD)

1. *Principle and Applicability.*

1.1 Air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m.³/min.; 40 to 60 ft.³/min.) that allows suspended particles having diameters of less than 100 μm. (Stokes equivalent diameter) to pass to the filter surface. (*1*) Particles within the size range of 100 to 0.1μm. diameter are ordinarily collected on glass fiber filters. The mass concentration of suspended particulates in the ambient air (μg./m.³) is computed by measuring the mass of collected particulates and the volume of air sampled.

1.2 This method is applicable to measurement of the mass concentration of suspended particulates in ambient air. The size of the sample collected is usually adequate for other analyses.

2. *Range and Sensitivity.*

2.1 When the sampler is operated at an average flow rate of 1.70 m.³/min. (60 ft.³/min.) for 24 hours, an adequate sample will be obtained even in an atmosphere having concentrations of suspended particulates as low as 1 μg./m.³. If particulate levels are unusually high, a satisfactory sample may be obtained in 6 to 8 hours or less. For determination of average concentrations of suspended particulates in ambient air, a standard sampling period of 24 hours is recommended.

2.2 Weights are determined to the nearest milligram, airflow rates are determined to the nearest 0.03 m.³/min. (1.0 ft.³/min.), times are determined to the nearest 2 minutes, and mass concentrations are reported to the nearest microgram per cubic meter.

3. *Interferences.*

3.1 Particulate matter that is oily, such as photochemical smog or wood smoke, may block the filter and cause a rapid drop in airflow at a nonuniform rate. Dense fog or high humidity can cause the filter to become too wet and severely reduce the airflow through the filter.

3.2 Glass-fiber filters are comparatively insensitive to changes in relative humidity, but collected particulates can be hygroscopic. (*2*)

4. *Precision, Accuracy, and Stability.*

4.1 Based upon collaborative testing, the relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent. The corresponding value for multilaboratory variation (reproducibility of the method) is 3.7 percent. (*3*)

4.2 The accuracy with which the sampler measures the true average concentration depends upon the constancy of the airflow rate through the sampler. The airflow rate is affected by the concentration and the nature of the dust in the atmosphere. Under these conditions the error in the measured average concentration may be in excess of ±50 percent of the true average concentration, depending on the amount of reduction of airflow rate and on the variation of the mass concentration of dust with time during the 24-hour sampling period. (*4*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Sampler.* The sampler consists of three units: (1) the faceplate and gasket, (2) the filter adapter assembly, and (3) the motor unit. Figure B1 shows an exploded view of these parts, their relationship to each other, and how the are assembled. The sampler must be capable of passing environmental air through a 406.5 cm.² (63 in.²) portion of a clean 20.3 by 25.4 cm. (8- by 10-in.) glass-fiber filter at a rate of at least 1.70 m.³/min. (60 ft.³/min.). The motor must be capable of continuous operation for 24-hour periods with input voltages ranging from 110 to 120 volts, 50–60 cycles alternating current and must have third-wire safety ground. The housing for the motor unit may be of any convenient construction so long as the unit remains airtight and leak-free. The life of the sampler motor can be extended by lowering the voltage by about 10 percent with a small "buck or boost" transformer between the sampler and power outlet.

5.1.2 *Sampler Shelter.* It is important that the sampler be properly installed in a suitable shelter. The shelter is subjected to extremes of temperature, humidity, and all types of air pollutants. For these reasons the materials of the shelter must be chosen carefully. Properly painted exterior plywood or heavy gauge aluminum serve well. The sampler must be mounted vertically in the shelter so that the glass-fiber filter is parallel with the ground. The shelter must be provided with a roof so that the filter is protected from precipitation and debris. The internal arrangement and configuration of a suitable shelter with a gable roof are shown in Figure B2. The clearance area between the main housing and the roof at its closest point should be 580.5±193.5 cm.² (90±30 in.²). The main housing should be rectangular, with dimensions of about 29 by 36 cm. (11½ by 14 in.).

5.1.3 *Rotameter.* Marked in arbitrary units, frequently 0 to 70, and capable of being calibrated. Other devices of at least comparable accuracy may be used.

5.1.4 *Orifice Calibration Unit.* Consisting of a metal tube 7.6 cm. (3 in.) ID and 15.9 cm. (6¼ in.) long with a static pressure tap 5.1 cm. (2 in.) from one end. See Figure B3. The tube end nearest the pressure tap is flanged to about 10.8 cm. (4¼ in.) OD with a male thread of the same size as the inlet end of the high-volume air sampler. A single metal plate 9.2 cm. (3⅝ in.) in diameter and 0.24 cm. (3/32 in.) thick with a central orifice 2.9 cm. (1⅛ in.) in diameter is held in place at the air inlet end with a female threaded ring. The other end of the tube is flanged to hold a loose female threaded coupling, which screws onto the inlet of the sampler. An 18-hole metal plate, an integral part of the unit, is positioned between the orifice and sampler to simulate the resistance of a clean glass-fiber filter. An orifice calibration unit is shown in Figure B3.

5.1.5 *Differential Manometer.* Capable of measuring to at least 40 cm. (16 in.) of water.

5.1.6 *Positive Displacement Meter.* Calibrated in cubic meters or cubic feet, to be used as a primary standard.

5.1.7 *Barometer.* Capable of measuring atmospheric pressure to the nearest mm.

5.2 *Analysis.*

5.2.1 *Filter Conditioning Environment.* Balance room or desiccator maintained at 15° to 35°C. and less than 50 percent relative humidity.

5.2.2 *Analytical Balance.* Equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm. (8- by 10-in.) filters and having a sensitivity of 0.1 mg.

5.2.3 *Light Source.* Frequently a table of the type used to view X-ray films.

5.2.4 *Numbering Device.* Capable of printing identification numbers on the filters.

6. *Reagents.*

6.1 *Filter Media.* Glass-fiber filters having a collection efficiency of at least 99 percent for particles of 0.3 μm. diameter, as measured by the DOP test, are suitable for the quantitative measurement of concentrations of suspended particulates, (5) although some other medium, such as paper, may be desirable for some analyses. If a more detailed analysis is contemplated, care must be exercised to use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Filter Preparation.* Expose each filter to the light source and inspect for pinholes, particles, or other imperfections. Filters with visible imperfections should not be used. A small brush is useful for removing particles. Equilibrate the filters in the filter conditioning environment for 24 hours. Weigh the filters to the nearest milligram; record tare weight and filter identification number. Do not bend or fold the filter before collection of the sample.

7.1.2 *Sample Collection.* Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Install a numbered, preweighed, glass-fiber filter in position (rough side up), replace the faceplate without disturbing the filter, and fasten securely. Undertightening will allow air leakage, overtightening will damage the sponge-rubber faceplate gasket. A very light application of talcum powder may be used on the sponge-rubber faceplate gasket to prevent the filter from sticking. During inclement weather the sampler may be removed to a protected area for filter change. Close the roof of the shelter, run the sampler for about 5 minutes, connect the rotameter to the nipple on the back of the sampler, and read the rotameter ball with rotameter in a vertical position. Estimate to the nearest whole number. If the ball is fluctuating rapidly, tip the rotameter and slowly straighten it until the ball gives a constant reading. Disconnect the rotameter from the nipple; record the initial rotameter reading and the starting time and date on the filter folder. (The rotameter should never be connected to the sampler except when the flow is being measured.) Sample for 24 hours from midnight to midnight and take a final rotameter reading. Record the final rotameter reading and ending time and date on the filter folder. Remove the faceplate as described above and carefully remove the filter from the holder, touching only the outer edges. Fold the filter lengthwise so that only surfaces with collected particulates are in contact, and place in a manila folder. Record on the folder the filter number, location, and any other factors, such as meteorological conditions or razing of nearby buildings, that might affect the results. If the sample is defective, void it at this time. In order to obtain a valid sample, the high-volume sampler must be operated with the same rotameter and tubing that were used during its calibration.

7.2 *Analysis.* Equilibrate the exposed filters for 24 hours in the filter conditioning environment, then reweigh. After they are weighed, the filters may be saved for detailed chemical analysis.

7.3 *Maintenance.*

7.3.1 *Sampler Motor.* Replace brushes before they are worn to the point where motor damage can occur.

7.3.2 *Faceplate Gasket.* Replace when the margins of samples are no longer sharp. The gasket may be sealed to the faceplate with rubber cement or double-sided adhesive tape.

7.3.3 *Rotameter.* Clean as required, using alcohol.

8. *Calibration.*

8.1 *Purpose.* Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual airflow with the orifice calibration unit. Before the orifice calibration unit can be used to calibrate the rotameter, the orifice calibration unit itself must be calibrated against the positive displacement primary standard.

8.1.1 *Orifice Calibration Unit.* Attach the orifice calibration unit to the intake end of the positive displacement primary standard and attach a high-volume motor blower unit to the exhaust end of the primary standard. Connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit and leave the other end open to the atmosphere. Operate the high-volume motor blower unit so that a series of different, but constant, airflows (usually six) are obtained for definite time periods. Record the reading on the differential manometer at each airflow. The different constant airflows are obtained by placing a series of loadplates, one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure at the inlet of the primary standard below atmospheric; therefore, a correction must be made for the increase in volume caused by this decreased inlet pressure. Attach one end of a second differential manometer to an inlet pressure tap of the primary standard and leave the other open to the atmosphere. During each of the constant airflow measurements made above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure and temperature. Correct the measured air volume to true air volume as directed in 9.1.1, then obtain true airflow rate, Q, as directed in 9.1.3. Plot the differential manometer readings of the orifice unit versus Q.

8.1.2 *High-Volume Sampler.* Assemble a high-volume sampler with a clean filter in place and run for at least 5 minutes. Attach a rotameter, read the ball, adjust so that the ball reads 65, and seal the adjusting mechanism so that it cannot be changed easily. Shut off motor, remove the filter, and attach the orifice calibration unit in its place. Operate the high-volume sampler at a series of different, but constant, airflows (usually six). Record the reading of the differential manometer on the orifice calibration unit, and record the readings of the rotameter at each flow. Measure atmospheric pressure and temperature. Convert the differential manometer reading to m.³/min., Q, then plot rotameter reading versus Q.

8.1.3 *Correction for Differences in Pressure or Temperature.* See Addendum B.

9. *Calculations.*

9.1 *Calibration of Orifice.*

9.1.1 *True Air Volume.* Calculate the air volume measured by the positive displacement primary standard.

$$V_a = \frac{(P_a - P_m)}{P_a}(V_m)$$

V_a = True air volume at atmospheric pressure, m.³
P_a = Barometric pressure, mm. Hg.
P_m = Pressure drop at inlet of primary standard, mm. Hg.
V_m = Volume measured by primary standard, m.³

9.1.2 *Conversion Factors.*
Inches Hg. × 25.4 = mm. Hg.
Inches water × 73.48 × 10^{-3} = inches Hg.
Cubic feet air × 0.0284 = cubic meters air.

9.1.3 *True Airflow Rate.*

$$Q = \frac{V_a}{T}$$

Q = Flow rate, m.³/min.
T = Time of flow, min.

9.2 *Sample Volume.*

9.2.1 *Volume Conversion.* Convert the initial and final rotameter readings to true airflow rate, Q, using calibration curve of 8.1.2.

9.2.2 *Calculate volume of air sampled*

$$V = \frac{Q_1 Q_f}{2} \times T$$

V = Air volume sampled, m.³
Q_1 = Initial airflow rate, m.³/min.
Q_f = Final airflow rate, m.³/min.
T = Sampling time, min.

9.3 *Calculate mass concentration of suspended particulates*

$$S.P. = \frac{(W_f - W_i) \times 10^6}{V}$$

S.P. = Mass concentration of suspended particulates, μg/m.³
W_i = Initial weight of filter, g.
W_f = Final weight of filter, g.
V = Air volume sampled, m.³
10^6 = Conversion of g. to μg.

10. *References.*

(1) Robson, C. D., and Foster, K. E., "Evaluation of Air Particulate Sampling Equipment", *Am. Ind. Hyg. Assoc. J. 24,* 404 (1962).

(2) Tierney, G. P., and Conner, W. D., "Hygroscopic Effects on Weight Determinations of Particulates Collected on Glass-Fiber Filters", *Am. Ind. Hyg. Assoc. J. 28,* 363 (1967).

(3) Unpublished data based on a collaborative test involving 12 participants, conducted under the direction of the Methods Standardization Services Section of the National Air Pollution Control Administration, October, 1970.

(4) Harrison, W. K., Nader, J. S., and Fugman, F. S., "Constant Flow Regulators for High-Volume Air Sampler", *Am. Ind. Hyg. Assoc. J. 21,* 114–120 (1960).

(5) Pate, J. B., and Tabor, E. C., "Analytical Aspects of the Use of Glass-Fiber Filters for the Collection and Analysis of Atmospheric Particulate Matter", *Am. Ind. Hyg. Assoc. J. 23*, 144–150 (1962).

ADDENDA

A. *Alternative Equipment.*

A modification of the high-volume sampler incorporating a method for recording the actual airflow over the entire sampling period has been described, and is acceptable for measuring the concentration of suspended particulates (Henderson, J. S., Eighth Conference on Methods in Air Pollution and Industrial Hygiene Studies, 1967, Oakland, Calif.). This modification consists of an exhaust orifice meter assembly connected through a transducer to a system for continuously recording airflow on a circular chart. The volume of air sampled is calculated by the following equation:

$$V = Q \times T.$$

Q = Average sampling rate, m.³/min.
T = Sampling time, minutes.

The average sampling rate, Q, is determined from the recorder chart by estimation if the flow rate does not vary more than 0.11 m.³/min. (4 ft.³/min.) during the sampling period. If the flow rate does vary more than 0.11 m.³ (4 ft.³/min.) during the sampling period, read the flow rate from the chart at 2-hour intervals and take the average.

B. *Pressure and Temperature Corrections.*

If the pressure or temperature during high-volume sampler calibration is substantially different from the pressure or temperature during orifice calibration, a correction of the flow rate, Q, may be required. If the pressures differ by no more than 15 percent and the temperatures differ by no more than 100 percent (°C), the error in the uncorrected flow rate will be no more than 15 percent. If necessary, obtain the corrected flow rate as directed below. This correction applies only to orifice meters having a constant orifice coefficient. The coefficient for the calibrating orifice described in 5.1.4 has been shown experimentally to be constant over the normal operating range of the high-volume sampler (0.6 to 2.2 m.³/min.; 20 to 78 ft.³/min.). Calculate corrected flow rate:

$$Q_2 = Q_1\left[\frac{T_2 P_1}{T_1 P_2}\right]^{1/2}$$

Q_2 = Corrected flow rate, m.³/min.
Q_1 = Flow rate during high-volume sampler calibration (Section 8.1.2), m.³/min.
T_1 = Absolute temperature during orifice unit calibration (Section 8.1.1), °K or °R.
P_1 = Barometric pressure during orifice unit calibration (Section 8.1.1), mm. Hg.
T_2 = Absolute temperature during high-volume sampler calibration (Section 8.1.2), °K or °R.
P_2 = Barometric pressure during high-volume sampler calibration (Section 8.1.2), mm. Hg.

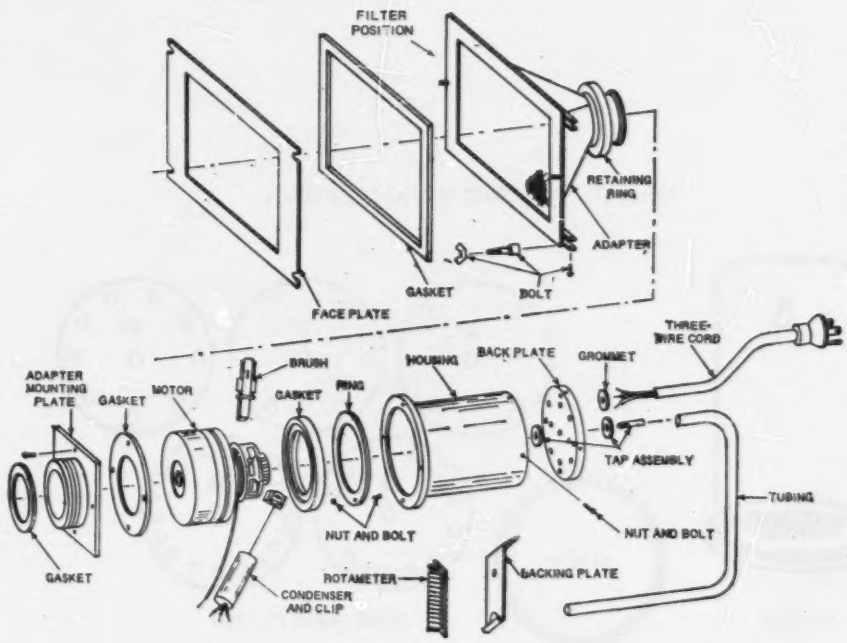

Figure B1. Exploded view of typical high-volume air sampler parts.

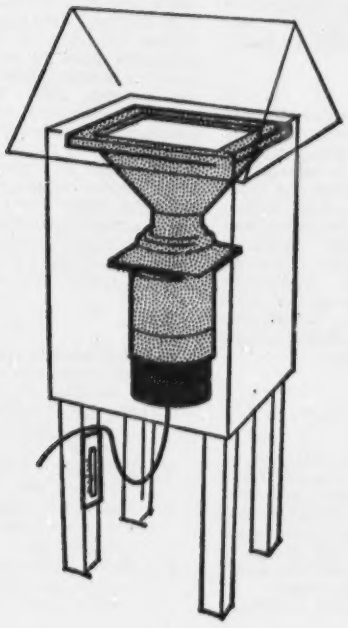

Figure B2. Assembled sampler and shelter.

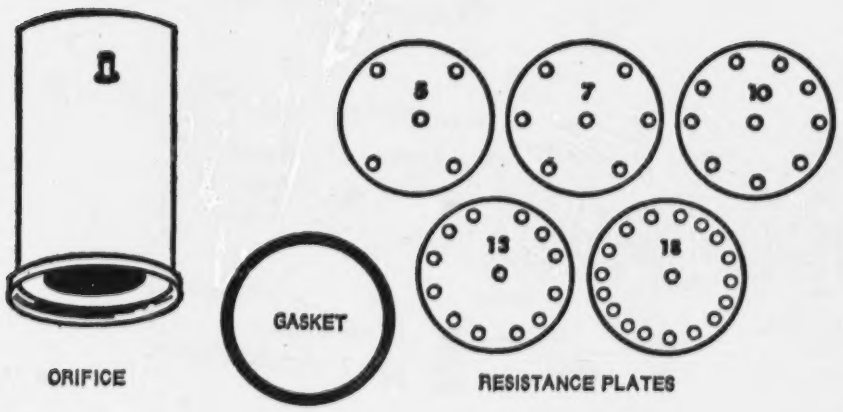

Figure B3. Orifice calibration unit.

APPENDIX B
STATISTICAL METHODS

1. Data Transformation

The total suspended particulate measurement has often been assumed to be log-normally distributed. This is generally advisable whenever the standard deviation tends to fluctuate systematically with its respective mean. The simple logarithmic transformation is widely applicable but not necessarily the only one to use.

Bartlett's test[1]* for homogeneity of variance was applied to both transformed and raw data. The null hypothesis that the variances for each day are homogeneous was rejected (95 percent level of significance) for the full set of raw data and accepted for the full set of transformed data. Therefore, in performing the analysis of variance and all subsequent analyses, the logarithms (base 10) of the total suspended particulate measurements were used, since they can be assumed to be normally distributed. The transformed data are shown in Table B-I.

2. Missing Data

Missing data in the analysis of variance always pose a problem, but, fortunately, there was only one data gap and a simple approach was possible. The method[2] consists of inserting an estimate of the missing observation, so chosen to minimize the residual variance. The inserted value makes no contribution to the residual sum of squares, and it is unlikely to have any serious effect on the conclusions. Application of the method yielded an estimate equivalent to approximately 82 $\mu g/m^3$, but it should be emphasized that this value does not represent an observation. It allows an approximation of the results obtained by a less powerful nonorthogonal analysis of the incomplete data.

TABLE B-I. SUMMARY OF DATA FOR ALL LABORATORIES, WITH LOGARITHMIC TRANSFORMATION

Laboratory Code Number	Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation
222	2.1399	1.9138*	1.9395	2.0569	2.0125	0.1053
311	2.0969	1.9031	1.9138	2.0531	1.9917	0.0979
320	2.1072	1.8573	1.9085	2.0492	1.9806	0.1171
341	2.1004	1.8751	1.9191	2.0569	1.9879	0.1078
345	2.1038	1.8921	1.9395	2.0934	2.0072	0.1074
509	2.1072	1.8692	1.9345	2.0828	1.9984	0.1151
572	2.1072	1.9138	1.9243	2.0492	1.9986	0.0950
575	2.0334	1.8633	1.8573	1.9685	1.9306	0.0854
578	2.1004	1.8865	1.9191	2.0453	1.9878	0.1016
600	2.0969	1.8573	1.9031	2.0414	1.9747	0.1130
787	2.0969	1.8808	1.9191	2.0682	1.9912	0.1072
799	2.1173	1.8808	1.9345	2.0792	2.0029	0.1133
Mean	2.1006	1.8828	1.9177	2.0537	1.9887	
Maximum	2.1399	1.9138	1.9395	2.0934	2.0125	0.1171
Minimum	2.0334	1.8573	1.8573	1.9685	1.9306	0.0854
Standard Deviation	0.0243	0.0199	0.0224	0.0314	0.0212	

*Data value substituted for missing data.

3. Linear Model Analysis

This experiment is an illustrative example of the nonavailability of known reference values. There is no knowledge of the true values for each of the materials (days). The alternate approach[3,4] is to use the mean of all laboratories for each day to replace the unknown reference values. These reference values may be seen in Table B-I. The assumption is made that systematic differences exist between sets of measurements made by the same observer at different times, and that these systematic differences are linear functions of the magnitude of the measurements. Hence, the scheme is called "the linear model." The linear model leads to a simple design, but requires a special method of statistical analysis, geared to the practical objectives of a collaborative test.

For each day, we may plot the measured values versus the reference value substitutes. The measured values should be a linear function of the reference values (all data normally distributed), and the points corresponding to each line may be represented by three parameters: a mean; a slope; and a quantity related to the deviation from linearity, the standard error of estimate. These parameters are determined by a least squares regression analysis. These results for the transformed data are shown in Table B-II which

*Superscript numbers in parentheses refer to the List of References at the end of this Appendix.

TABLE B-II. ESTIMATES OF THE PARAMETERS OF THE STRAIGHT LINES CORRESPONDING TO THE VARIOUS LABORATORIES, LOGARITHMIC DATA TRANSFORMATION, ALL LABORATORIES

Laboratory Code Number	Mean	Slope	Standard Error of Estimate
222	2.0125	0.9929	0.0189
311	1.9917	0.9294	0.0110
320	1.9806	1.1150	0.0069
341	1.9879	1.0272	0.0047
345	2.0072	1.0122	0.0197
509	1.9984	1.0869	0.0191
572	1.9986	0.8998	0.0131
575	1.9306	0.7966	0.0218
578	1.9878	0.9678	0.0049
600	1.9747	1.0762	0.0049
787	1.9912	1.0193	0.0098
799	2.0029	1.0768	0.0102
Mean	1.9887	1.0000	0.0141*
Maximum	2.0125	1.1150	0.0218
Minimum	1.9306	0.7966	0.0047

*Pooled Estimate.

was used to prepare Figure 1 found in Section III-E of this report. This figure shows the data for Laboratory 575 to be notably different from the other laboratories.

Control limits for the means and for the slopes may be computed, based upon the pooled estimate of standard error. Control charts, in standard deviation units, for these parameters are shown in Figures B-1 and B-2. No control limits are possible for the standard errors of estimate which are shown in Figure B-3. In Figure B-4, the individual slopes are plotted versus their respective means. The mean for Laboratory 575 is off scale in Figure B-1, and the atypical point in Figure B-4 is Laboratory 575.

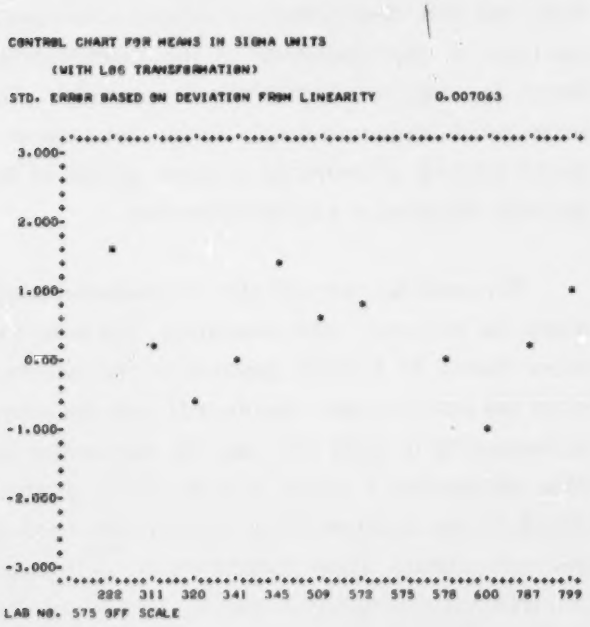

FIGURE B-1. COMPUTER PLOT OF CONTROL CHART FOR MEANS, ALL LABORATORIES

It is now obvious that the results of Laboratory 575 are significantly different. Dixon's Q test[5] indicates Laboratory 575 to be an outlier, at the 99 percent level of significance, for all but the second day. As a result, the data in Laboratory 575 were omitted from all subsequent analysis.

The data were reprocessed omitting Laboratory 575, and the results are shown in Table B-III.

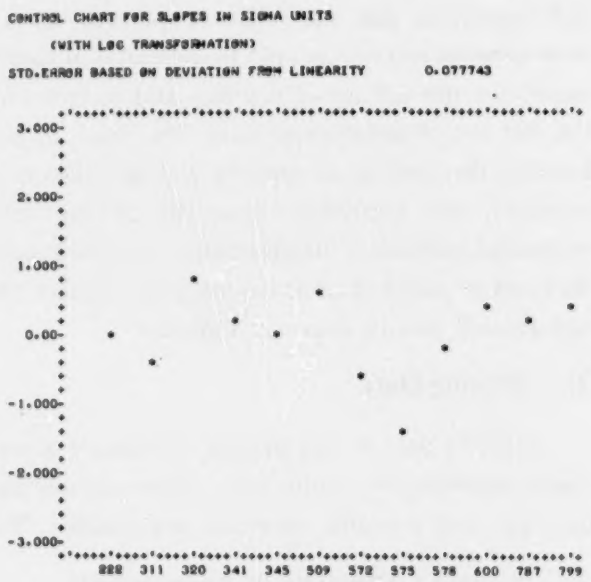

FIGURE B-2. COMPUTER PLOT OF CONTROL CHART FOR SLOPES, ALL LABORATORIES

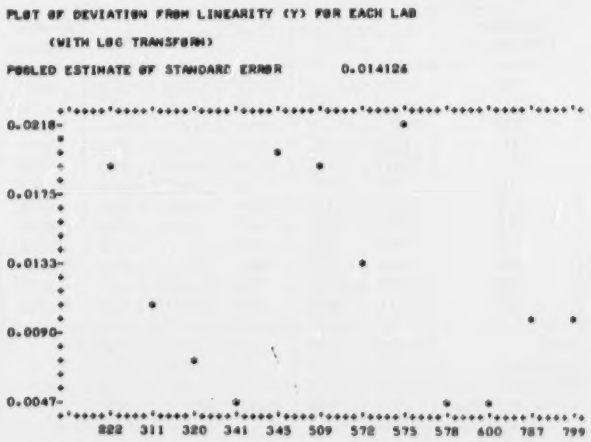

FIGURE B-3. COMPUTER PLOT OF DEVIATION FROM LINEARITY, ALL LABORATORIES

FIGURE B-4. COMPUTER PLOT OF SLOPES VERSUS MEANS, ALL LABORATORIES

Although the individual data for each remaining laboratory are the same as shown in Table B-I, there are important differences in the summary statistics. New reference values have been established, and the standard deviations are more uniform.

TABLE B-III. SUMMARY OF DATA, OMITTING LABORATORY 575, WITH LOGARITHMIC TRANSFORMATION

Statistic	Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation
Mean	2.1067	1.8845	1.9232	2.0614	1.9940	
Maximum	2.1399	1.9138	1.9395	2.0934	2.0125	0.1171
Minimum	2.0969	1.8573	1.9031	2.0414	1.9747	0.0950
Standard Deviation	0.0126	0.0199	0.0124	0.0171	0.0113	

Using the new reference values and the remaining 11 laboratories, a final data analysis using the linear model was made. The results of the regression analysis are shown in Table B-IV, which is analogous to Table B-II, but only the individual means are the same. The slopes and the standard errors of estimate are more uniform.

Control limits for the means and for the slopes may again be computed. The control chart for means is not shown because it is practically the same as Figure B-1 with the point for Laboratory 575 omitted. The standard error based on deviation from linearity is lower and is 0.006435, which, coupled with a slightly higher average mean, results in shifting each point in Figure B-1 downward about 0.4 unit. The control chart for slopes is also not shown because it is practically the same as Figure B-2 with the point for Laboratory 575 omitted. The standard error based on deviation from linearity is lower and is 0.06954, and, of course, the range of slopes is substantially reduced. The net effect is to move each point in Figure B-2 downward approximately 0.2 unit.

TABLE B-IV. ESTIMATES OF THE PARAMETERS OF THE STRAIGHT LINES CORRESPONDING TO THE VARIOUS LABORATORIES, OMITTING LABORATORY 575, LOGARITHMIC DATA TRANSFORMATION

Laboratory Code Number	Mean	Slope	Standard Error of Estimate
222	2.0125	0.9729	0.0205
311	1.9917	0.9113	0.0124
320	1.9806	1.0948	0.0063
341	1.9879	1.0089	0.0028
345	2.0072	0.9955	0.0181
509	1.9984	1.0691	0.0170
572	1.9986	0.8817	0.0149
578	1.9878	0.9496	0.0064
600	1.9747	1.0566	0.0047
787	1.9912	1.0013	0.0085
799	2.0029	1.0582	0.0081
Mean	1.9940	1.0000	0.0129*
Maximum	2.0125	1.0948	0.0205
Minimum	1.9747	0.8817	0.0028

*Pooled Estimate.

The control chart for standard errors is similar in appearance to Figure B-3 with the point for Laboratory 575 omitted, and, therefore, is not shown. Comparing the standard errors of estimate in Tables B-II and B-IV, it can be seen that the pooled estimate of standard errors is reduced, but that the range is approximately the same after elimination of Laboratory 575.

The plot of slopes versus means is shown in Figure B-5 which is analogous to Figure B-4, but indicates that the deletion of the single atypical point due to Laboratory 575 results in a substantial reduction in the correlation between the slopes and the means. This is apparent both visually as well as from the correlation coefficients shown in Figures B-4 and B-5.

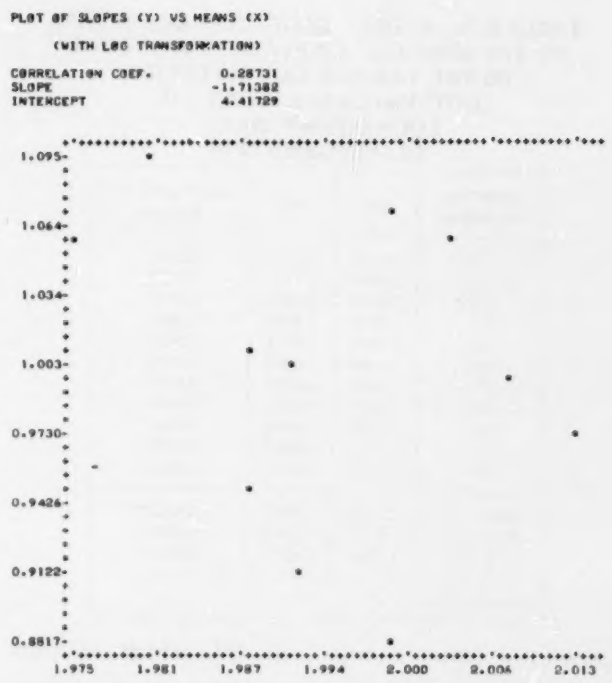

FIGURE B-5. COMPUTER PLOT OF SLOPES VERSUS MEANS, OMITTING LABORATORY 575

No further elimination of outliers is required, and the following conclusions can now be drawn:

- There is no significant variation in the means and slopes among the eleven laboratory lines which cannot be entirely explained by the scatter due to the deviation from linearity.

- There is no correlation between the slopes and the means of the individual lines.

4. Analysis of Variance

The general model for the analysis of the results, classified according to two criteria, laboratories and materials (simulated by different days), is:(6)

$$y_{ij} = A + L_i + M_j + (LM)_{ij}$$

where

y_{ij} ≡ an individual measurement

A ≡ overall average

L_i ≡ main effect of laboratory i

M_j ≡ main effect of material (day) j

$(LM)_{ij}$ ≡ interaction effect between laboratory i and material j and includes unknown replication error

i = 1, 2, 3 . . . p ≡ number of laboratories

j = 1, 2, 3 . . . q ≡ number of materials

A more meaningful analysis is obtained by partitioning the interaction term as follows:

$$(LM)_{ij} = (b_i - \overline{b})(c_j - \overline{c}) + d_{ij}$$

where the first term is the linear term in which b_i is the slope determined by the ith laboratory, $\overline{b}$ represents the slope of the average total suspended particulate (TSP) observed-versus-mean line (averaged over all laboratories), c_j represents the true TSP value for the jth material, and $\overline{c}$ represents the true mean TSP of all materials. The second term, d_{ij}, is the deviation from linear term. The linear term indicates the difference in slope of the line for a particular laboratory and the average slope for all laboratories, and the nonlinear term expresses the departures from linearity for this individual line.

Starting with the ordinary two-factor analysis of variance, the deviation from linear component of the interaction sum of squares can be computed.(7) The sum of squares for the linear component of interaction is then obtained by

TABLE B-V. ANALYSIS OF VARIANCE OMITTING LABORATORY 575, WITH LOGARITHMIC TRANSFORMATION

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
Laboratories	0.005126	10	0.000513
Days	0.376777	3	0.125592
Labs × Days	0.004874	30	0.000162
Linear	0.001562	10	0.000156
Concurrence	0.000129	1	0.000129
Nonconcurrence	0.001433	9	0.000159
Deviation from Linear	0.003313	20	0.000166

difference. For the sake of completeness, the linear component may be further partitioned into a concurrence and a nonconcurrence term,[8] although it is apparent that no appreciable correlation exists between the means and the slopes of the laboratory lines. This is done without further explanation and is shown in Table B-V. The purpose for making the analysis of variance is to derive the components of variance. These components are computed from Table B-V and are shown in Table III in Section III-E of this report.

LIST OF REFERENCES

1. Dixon, Wilfrid J. and Massey, Frank J., Jr., **Introduction to Statistical Analysis**, Chapter 10, McGraw-Hill Book Company, Inc., New York, pp 179-180 (1957).

2. Bennett, Carl A. and Franklin, Norman L., **Statistical Analysis in Chemistry and the Chemical Industry**, John Wiley and Sons, Inc., New York, pp 379-385 (1954).

3. ASTM Manual for Conducting an Interlaboratory Study of a Test Method, ASTM STP No. 335, *Am. Soc. Testing & Mats.* (1963).

4. Mandel, John and Lashof, T.W., "The Interlaboratory Evaluation of Testing Methods," ASTM Bulletin, No. 239, p 53 (TP133) (July 1959).

5. Recommended Practice for Dealing with Outlying Observations, ASTM Designation: E178-68, Book of ASTM Standards, Part 30 (1968).

6. ASTM STP No. 335, op. cit., p 27.

7. Ibid, p 34.

8. Ibid, p 28.